ACIDIC PRECIPITATION IN ONTARIO STUDY

AN OVERVIEW:

THE EVENT WET/DRY DEPOSITION NETWORK

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1. INTRODUCTION

The Air Resources Branch currently operates two networks under the auspices of the Acidic Precipitation in Ontario Study (APIOS). Both networks were designed with the general objective of quantifying wet and dry deposition across the province of Ontario. The specific objectives of the two networks differ slightly and are described in detail in their individual network overviews.

The networks referred to are the APIOS Cumulative Wet/Dry Deposition Network and the APIOS Event Wet/Dry Deposition Network. The former collects cumulative samples on a 28-day cycle (monthly basis since the network inception to December, 1981) for the determination of long term wet/dry deposition patterns; the latter collects precipitation and air filter samples on a daily basis for the determination of both wet and dry short term deposition.

It should be emphasized that since both networks measure deposition, the difference between the two is related to the sampling period. Specifically, event (used interchangeably with daily sampling by some researchers) sampling allows one to investigate the characteristics of deposition events and to determine the origin of the pollutants deposited in these events. Cumulative sampling, on the other hand, provides information only on long term deposition patterns.

Details of Cumulative Network are given elsewhere in an overview entitled "The Acidic Precipitation in Ontario Study (APIOS) Cumulative Wet/Dry Deposition Network" available from the Air Resources Branch. No further discussion of this network is given in this document.

The Event Wet/Dry Deposition Network described herein consists of two components - one for the measurement of wet deposition and the other for the measurement of dry deposition. The following sections provide an overview of these two network components. For ease of presentation, details of the wet

deposition sampling are described independently under the heading "Daily Wet Deposition Network" and the dry deposition sampling under "Daily Dry Deposition Network". Details beyond those described herein can be obtained by contacting the Air Resources Branch directly.

2. NETWORK OBJECTIVES

2.1 Daily Wet Deposition Network:

The objectives of this network are twofold:

(1) To study the chemical composition, frequency and intensity of acidic precipitation episodes in the province.

(2) To determine the wet deposition of acid - related materials associated with air masses originating from different directions and, hence, from different emission source regions.

2.2 Daily Dry Deposition Network:

The objectives of this network are also two-fold:

(1) To determine the amount and origin of airborne acid-related pollutants available for deposition in Ontario on a daily basis.

(2) To estimate dry deposition rates of these pollutants on a daily basis by using the airborne concentrations and appropriate deposition velocity values in the relationship: deposition rate = deposition velocity x concentration. Also, to determine the dry deposition of acid - related materials associated with air masses originating in different sectors.

3. NETWORK DESIGN

3.1 Daily Wet Deposition Network:

In order to fulfill its stated objectives, the design of the APIOS Daily Wet Deposition Network was based on the following requirements:

(1) to make measurements on a daily basis

(2) to locate samplers of spatial scales varying for local to regional to provincial.

(3) to give special emphasis to sampling in areas of known high acidic deposition and/or high sensitivity to acidic deposition.

(4) to locate the sampling stations along the prevailing flow direction for Ontario and along the Canada-United States border.

Four general areas of Ontario were chosen for the sampling program, namely the London, Kingston, Dorset and Atikokan areas. The former three are aligned along the prevailing flow direction for the southern part of Ontario and have significant levels of precipitation acidity (based on historical data). Dorset is an area of known acid sensitive lakes and is the focus of a great deal of study; London and Kingston, being located close to the U.S. border, can be used to determine directly the amount of deposition associated with emissions from the United States. The Atikokan area was chosen to monitor background concentrations of pollutants prior to the 1984 start-up of a coal-fired generating station at Atikokan. As well, within the zone of influence of the Atikokan generator lie the acid-sensitive lakes of the Boundary Waters Canoe Area of northern Minnesota.

Each of these sampling areas is designed to have 4 event precipitation collection sites. The 4 samplers within each cluster are separated into 2 groups of 2 samplers each. Between each group is to be a distance of 50 to 100 km. Within each group,the samplers are to be 5 to 10 km apart. At one site, two sampling instruments are to run side-by-side for the measurement of precision.

3.2 Daily Dry Deposition Network:

One of the daily precipitation monitoring sites in each of the London, Kingston, Dorset and Atikokan areas was chosen as a Daily Dry Deposition Network site. The number of samplers in each region is significantly smaller than that for precipitation sampling because of smaller spatial variability in air quality data.

4. NETWORK SAMPLING LOCATIONS AND SITING CRITERIA

4.1 Daily Wet Deposition Network:

Based on the design criteria outlined in the previous section, the London, Kingston, Dorset and Atikokan areas were inspected for proper sampling sites. Determining the actual locations involved fulfilling both the aforementioned spatial requirements as well as specific requirements on the suitability of sites of proper precipitation sampling. These latter requirements are discussed in detail elsewhere (1,2) but are summarized briefly as follows: precipitation sampling sites must be located away from local sources of pollution, e.g. industrial activity, urban areas, airports, highways etc; the sampling instrument itself must be located at a site which has little or no potential for contaminating the samples, i.e., it must be clear of obstructions (trees, buildings); must not have roads or other site-specific sources of contamination nearby, e.g. sewage treatment plants, agricultural activity, heating plants, gravel pits and salt or sand piles, and gardens, etc.

Four sites in each of the London, Kingston, Dorset and Atikokan areas were selected according to these criteria. Some of the sites are located at Ministry of Natural Resources' parks and regional conservation authority areas, while others are on personal property. The actual sampling locations are shown in Figure 1 and listed in Table 1. It should be noted that locating this number of sites

which satisfy all of the design and site selection criteria was extremely difficult particularly in the sparsely-populated region of northwestern Ontario. A lack of good sampling sites in this area has extended the desired range separating the pairs of samplers.

4.2 Daily Dry Deposition Network:

The site selection criteria for the air quality samplers is similar to those for precipitation samplers. However, only one sampler is located in each of the principal areas. They are located at Longwoods Conservation Area near London, Charleston Lake Provincial Park near Kingston, the MOE laboratory site at Dorset, and at the United States-Environmental Protection Agency's Fernberg Road meteorological site near Ely, Minnesota.

5. INSTRUMENTATION

5.1 Daily Wet Deposition Network:

Each daily deposition monitoring site is instrumented with a wet deposition collector (of which the sample is analysed for its chemical composition) and a Atmospheric Environment Service standard precipitation depth gauge, used to obtain a true depth of rainfall measurement.

For the months in which rain is collected primarily (May through October) the precipitation collector used is an Aerochem Metrics Model 301 Automatic Deposition Collector. The large surface area of the collection vessel and its high collection efficiency for rainfall make it ideal for this application. Each Aerochem Metrics sampler is supplied with a high-density polyethylene bucket for collecting rainfall. Collection of rainfall is done in disposable polyethylene bags inserted

into the buckets. This procedure eliminates the need for washing the vessel after each event and will reduce sample handling. The Aerochem Metrics collector is complemented by an Atmospheric Environment Service standard rain gauge, so that an accurate measurement of rainfall is obtained.

For the months which snow and/or rain are collected (November through April), the Aerochem Metrics deposition collector is replaced by a sampler known as the Sudbury Environmental Study (SES) - type collecter. This collector consists of a large-mouth (diameter ~47 cm) bucket with a polyetheylene bag insert. The bag is replaced daily so that each sample actually represents a 24-hour bulk measurement rather than a true wet-only measurement. Because of the snow cover and the stringent site selection criteria applied, it is expected that dry deposition would be minimal. Each SES-type collector is accompanied by a standard nipher-shielded snow gauge similar to that used by the Atmospheric Environment Service. This latter gauge provides an accurate daily measurement of snow depth.

At each of the primary event sites (i.e. Longswoods, Charleston Lake, Dorset and Fernberg) a Fisher-Porter rain guage is installed to provide information about the frequency, intensity and duration of precipitation events.

It should be noted that the SES-type sampler was chosen over the Aerochem Metrics sampler because of its better suitability for winter sampling. The Aerochem Metrics sampler has a relatively low collection efficiency for snow. The large collection area and the lower diameter-to-length ratio (which is related to the collection efficiency) of the SES collector provide better collection efficiency and greater precipitation volumes for laboratory analysis. Also, sensitivity and design problems with the Aerochem Metrics sampler for winter sampling were observed in the past.

5.2 Daily Dry Deposition Network:

The instrumentation at each Daily Dry Deposition Network site consists of an air filtration system for the measurement of ambient concentrations of sulfur

and nitrogen compounds. It consists of a set of multi-stage filter packs, a flow controller/time sequencer and a 10 m tower. Within this system, specific filter types are used to sample for specific compounds.

Nine filter packs are mounted at the top of the 10 m tower once per week. Seven of the nine packs sample for 24 hours each during a typical week (the eighth one is also used when an extension to the eighth sampling day is necessary). The ninth pack remains passive (the passive value is used to correct for background concentrations).

The filter packs used in the network are modified 'Swinnex' two-stage, 47 mm, polypropylene units manufactured by Millipore Corporation. Each filter pack samples for 24 hours (commencing at 0700 EST) at a flow rate of 25 litres per minute. This flow rate is maintained by a Gast, heavy-duty diaphragm pump and is controlled by a Metrex Instruments Ltd. SAS8-25 Sequential Air Sampler. This latter instrument is designed to be connected to the 8 active filter packs and will automatically sequence through the filter packs at 24-hour intervals. The associated 24-hour total volumetric flow through each filter pack is automatically recorded on digital counters.

Individual filter packs are loaded with 3 types of filters, each type specific for certain pollutants. The upstream filter is a Membrana (Ghia) Corporation 47 mm, 2 um teflon filter which collects particulate sulfate, nitrate and ammonium. The teflon filter is followed by a Membrana (Ghia) Corporation 47 mm, 1 um nylon filter, used for the selective adsorption of vapor phase nitric acid. Both filters are loaded in the upstream stage of the filter pack and are in direct contact.

The final filter type is 50 mm Whatman 41 cellulose filter impregnated with a potassium carbonate/glycerol solution. This impregnating solution selectively absorbs sulfur dioxide (SO_2). Two of these filters are loaded in the downstream stage of the filter pack and are also in direct contact.

The filter pack sampling therefore provides daily measurements of

particulate-phase sulfate, nitrate and ammonium as well as vapor phase nitric acid and sulfur dioxide. There is some evidence that the speciation of the nitrogen compounds using this type of selective sampling is subject to errors because of adsorption, desorption and volatility properties of the compounds. It is felt, however, that the summation of the NO_3 and HNO_3 on the teflon and nylon filters (respectively) is an accurate measurement of total ambient nitrates.

6. SAMPLE COLLECTION AND HANDLING TECHNIQUES

6.1 Daily Wet Deposition Network:

For the purposes of this network, a daily precipitation sample is defined as that precipitation collected within a 24 hour period starting at 0800 hours local time of one day and ending at 0800 hours the following day.

The sampling protocol is as follows:

Every day at 0800 hours, the site operator at each station checks the sampler. For the Aerochem Metrics sampler, the sensor is activated and the collection vessel is inspected for sample. If no precipitation was collected, the collection vessel is left in place and the hood is returned to the closed position. The standard precipitaiton gauge is then inspected for precipitation. This provides a check on proper Aerochem Metrics sampler operation. If precipitation did occur and was collected in the Aerochem Metrics vessel (previously bucket, now bag insert), the vessel collection is removed and replaced by a clean one. Precipitation collected in the standard gauge is measured and noted. The Aerochem Metrics sample is then transferred to a 450 ml polystyrene sample bottle and stored in a refrigerator on site. For volumes greater than 450 ml, the excess is measured and discarded. All pertinent information is noted on a sample submission form which accompanies each sample. As part of a quality assurrance program, information regarding factors affecting the sample collected is recorded in a log book on site.

Handling procedures for the SES-type samplers are slightly different. Each day at 0800 hours the sampler is checked. However, regardless of whether precipitation was collected or not, the bag is removed and replaced by a clean new one. This ensures that the sample collected over 24 hours has no potential for contamination from previous days. The balance of the handling procedures are similar to those for the Aerochem Metrics sampler.

Samples are picked up weekly from the on-site operators by APIOS technicians responsible for the samplers in their area (samples from the more remote sites in northwestern Ontario are sent in to the regional MOE laboratory weekly). The samples are transported in coolers to a regional MOE laboratory. The samples are then weighed for determination of sample volume and a field pH is measured (if the volume exceeds 180 ml). The samples are shipped by courier service to the Air Resources Branch in Toronto. Again, they are packed in coolers and arrive the following day still cooled. In Toronto, the samples are logged in, stored in a cold room and then are delivered to the Water Quality Laboratory of the MOE Laboratory Services Branch in Rexdale as soon as possible after receipt.

The use of polyethylene bags in the daily network is emphasized because of their inherent advantages to quality control. Each bag represents a pristine collection vessel for each precipitation sample so that site-to-site variability in collection vessel cleaning procedures is eliminated. Laboratory analysis of the bags has been carried out and no adsorption or desorption of the inorganic constituents of interest (refer to 7.1) onto the bag surface has been observed.

6.2 Daily Dry Deposition Network:

The filter pack samples obtained in this network are collected over a 24-hour period beginning and ending at 0700 EST. The sampling protocol is as follows: Once per week an unexposed set of 9 filter packs is loaded with teflon, nylon and impregnated Whatman 41 filters and taken to the sampling site. At the site, the tower is lowered and the exposed filter packs are removed and bagged. The new filter packs are mounted on the tower and are elevated to 10 m. The flow

volumes for each of the exposed filter packs are read off the Metrex flow controller and the unit is reset for the new filter pack sampling.

At the regional MOE laboratory, the filter packs are unloaded and individual filters are bagged and labelled. The filters are then submitted to the Laboratory Services Branch for their respective analyses via the Air Resources Branch.

7. CHEMICAL ANALYSES

7.1 Daily Wet Deposition Network:

All daily precipitation samples are analysed for the following parameters (listed in descending order of priority): Volume, pH, acidity, $SO_4^=$, $N\text{-}NO_3^-$, $N\text{-}NH_4^+$, Cl^-, Na^+, K^+, Ca^{++}, Mg^{++}, and conductivity. The methods of analysis are given in Table 2. Analysis of trace metals is not done at present but will be done on a limited basis in the future.

7.2 Daily Dry Deposition Network:

The individual filters are analysed for the following parameters: $SO_4^=$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ from the teflon filters; $N\text{-}HNO_3$ from the nylon filters (as nitrate); SO_2 from the impregnated Whatman 41 filters (as $SO_4^=$). Methods of extraction and analysis are given in Table 3.

8. DATA HANDLING AND ANALYSIS

8.1 Daily Wet Depositon Network:

The reporting of chemical analysis data is structured such that laboratory-approved data is entered from the Laboratory Information System (LIS) into the Ministry's Sample Information System (SIS) data base. A particular submission's supporting field data is merged with its chemical data. Before a submission's

results are finalized, the data are screened, according primarily to chemical balance and excedence of range validation programs.

Analysis of the data are to include:

1. the calculation of daily wet deposition rates as the product of pollutant concentration times true precipitation depth.
2. the characterization of events with respect to precipitation chemistry, depth and deposition.
3. the correlation of daily deposition data with air parcel trajectories for the determination of the origin of the pollutants.

8.2 Daily Dry Deposition Network:

Data from this network undergo the same transfer and screening procedures as wet deposition data.

Analysis of these data will be similar to the wet deposition data with the exception that dry deposition rates will be calculated as the product of pollutant air concentration times published values of dry depositon velocity.

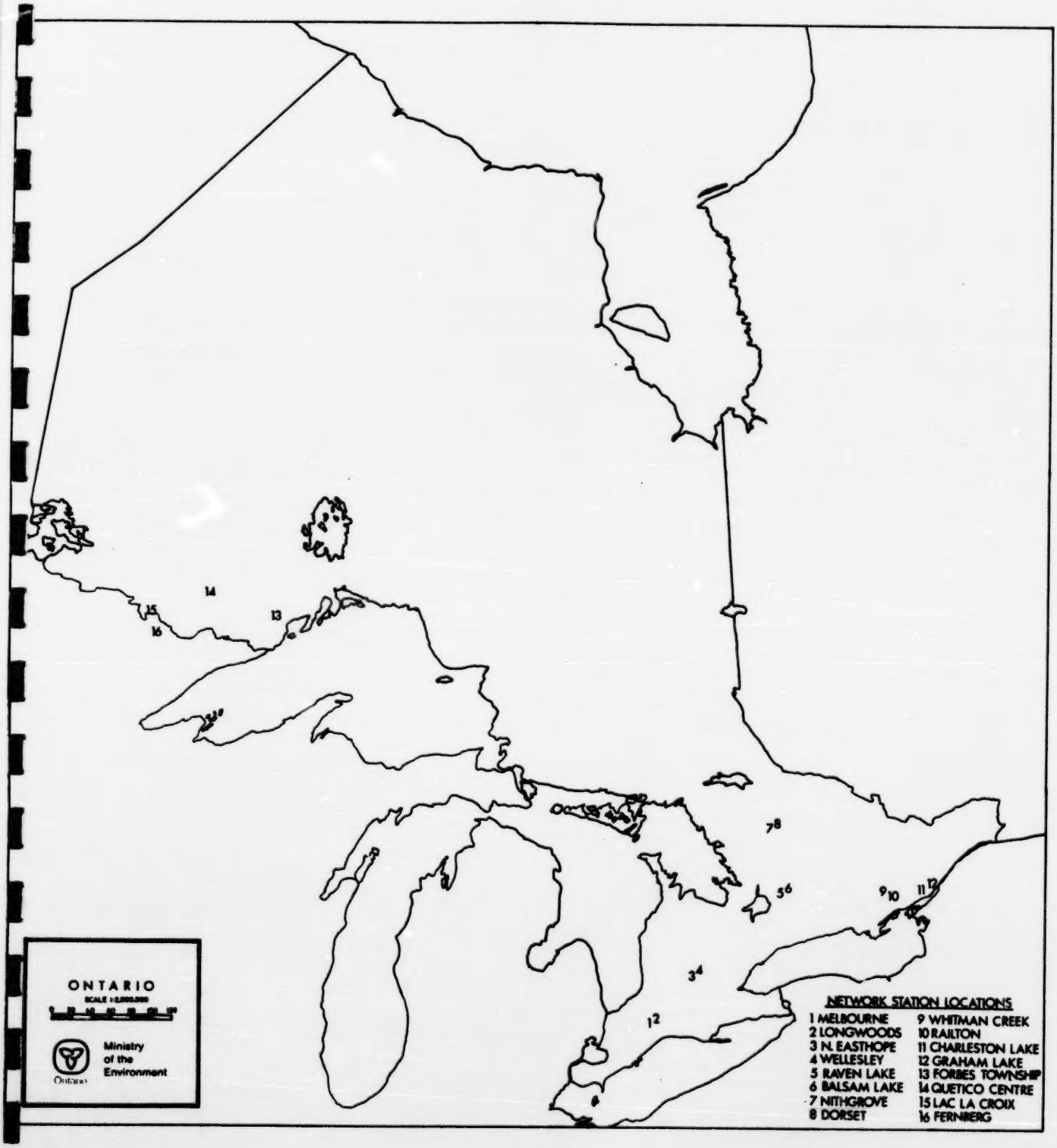
Additional analyses will be done to correlate concurrent wet and dry deposition data.

REFERENCES

(1) Vet, R.J., W.H. Chan and D.B. Orr, The Acidic Precipitation In Ontario Study (APIOS) Cumulative Wet/Dry Deposition Network, Air Resources Branch, June 1982 (revised version).

(2) Vet, R.J. APIOS Technicians Guide to Event Precipitation Site Inspection, Air Resources Branch, June, 1980.

Figure 1


ONTARIO
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NETWORK STATION LOCATIONS
1 MELBOURNE
2 LONGWOODS
3 N. EASTHOPE
4 WELLESLEY
5 RAVEN LAKE
6 BALSAM LAKE
7 NITHGROVE
8 DORSET
9 WHITMAN CREEK
10 RAILTON
11 CHARLESTON LAKE
12 GRAHAM LAKE
13 FORBES TOWNSHIP
14 QUETICO CENTRE
15 LAC LA CROIX
16 FERNBERG

Table 1

APOS EVENT WET/DRY DEPOSITION NETWORK SITE LOCATIONS

AREA	MOE REGION	STATION NAME	INSTRUMENTATION	ELEVATION (m above MSL)	LATITUDE (North)	LONGITUDE (West)	UTM COORDINATES (Northing)	(Easting)
London	Southwestern	Longwoods Conservations Area	Wet and Dry	239	42°53'	81°29'	4747850	460700
		Melbourne	Wet	213	42°47'	81°33'	4736850	454600
		North Easthope	Wet	375	43°24'	80°53'	4805650	508650
		Wellesley	Wet	344	43°28'	80°46'	4812650	519500
Dorset	Central	Dorset Lab	Wet and Dry	320	45°13'	78°56'	5009600	662450
		Nithgrove	Wet	325	45°12'	79°04'	5006800	651600
		Balsam Lake Provincial Park	Wet	259	44°38'	78°51'	4943400	670070
		Raven Lake	Wet	274	44°37'	78°54'	4941600	665750
Kingston	Southeastern	Charleston Lake Provincial Park	Wet and Dry	92	44°30'	76°03'	4927500	417150
		Graham Lake	Wet	130	44°35'	75°52'	4936750	431450
		Railton	Wet	137	44°29'	76°49'	4927200	355100
		Whitman Creek	Wet	137	44°29'	76°49'	4927200	355100
Atikokan	Northwestern	Fernberg	Wet and Dry	506	47°50'	91°52'	5316000	585000
		Lac la Croix	Wet	368	48°21'	92°12'	5356000	558200
		Forbes Twsp.	Wet	324	48°38'	89°37'	5388000	308000
		Quetico Centre	Wet	420	48°45'	91°12'	5399000	632000

Table 2

DAILY WET DEPOSITION NETWORK LABORATORY ANALYSES

Parameter	Analysis Method	Detection Limit (mg l^{-1})
pH (for H_f* determination)	Radiometer	0.01 pH units
Total Acidity (for H_t+ determination)	NaOH titration to pH 8.3; results presented as mg $CaCO_3$ l^{-1}	0.01
Conductivity	Radiometer	N/A
$SO_4^=$	Ion Chromatography	0.05
$N\text{-}NO_3^-$	Ion Chromatography	0.01
Cl^-	Ion Chromatography	0.01
$N\text{-}NH_4^+$	Automated phenate-hypochlorite method	0.002
Ca^{++}	Flame Atomic Absorption	0.01
Na^+	Flame Atomic Absorption	0.005
K^+	Flame Atomic Absorption	0.005
Mg^{++}	Flame Atomic Absorption	0.005

* H_f - free hydrogen ion concentration
+ H_t - total hydrogen ion concentration

Table 3

DAILY DRY DEPOSITION NETWORK LABORATORY ANALYSES

Parameter	Filter Type	Extraction Method	Analysis Method
$SO_4^=$	Teflon	15 minute ultrasonic bath in 25 ml distilled deionized water	Ion Chromatography
$N\text{-}NO_3^-$	Teflon	same as above	Ion Chromatography
$N\text{-}NH_4^+$	Teflon	same as above	Automated Phenate-Hypochlorite Colorimetry
$N\text{-}HNO_3$	Nylon	15 minute ultrasonic bath in 25 ml 3×10^{-3} N NaOH	Ion Chromatography (as NO_3^-)
SO_2	Impregnated Whatman 41 Cellulose	30 minute shaking in 50 ml 0.05% (v/v) hydrogen peroxide; followed by 15 minute shaking in 25 ml hydrogen peroxide; followed by making up to 100 ml with hydrogen peroxide.	Ion Chromatography (as $SO_4^=$)

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